

PHYTOTOXICOLOGY INVESTIGATION
OF SURFACE AND SUB-SURFACE
SOILS ON UNION STREET,
CAMBRIDGE, SEPTEMBER 24, 1991

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Phytotoxicology Section
Air Resources Branch
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BACKGROUND

Waste road construction material was utilized on residential properties on Union Street, Cambridge, as fill material in 1988. There were large quantities of asphalt intermixed with other fill material. This material was deposited around foundations and in excavated areas in both the front and back yards and often to considerable depth. The residents of 256 Union Street persistently outlined their health-related concerns to the Cambridge District, Ministry of the Environment (MOE) Office.

In August 1991, the MOE asked the City of Cambridge to remove the asphalt from the residential property to resolve the concerns of the complainants and to acknowledge the position of the District Office that asphalt was not an appropriate fill material in a residential area. The City agreed to the removal of asphalt that could be feasibly excavated from the property and asked neighbours in the row-housing development if they wanted asphalt removed from their properties. A public meeting was held on September 5, 1991 that was attended by property owners, the press and other interested public. At this meeting Larry Macdonnell, the MOE Area Supervisor, was asked to conduct testing to determine if the soil had been contaminated by leachate from the asphalt.

The Phytotoxicology Section of the MOE was asked by D.R. Ireland, District Officer, Cambridge District to conduct a soil sampling survey of the affected properties along Union Street. The formal request for sampling was received on September 18, 1991. Appropriate resident contacts were made by Ron McKnight (Environmental Officer-Cambridge) and soil sampling was conducted on September 24, 1991. The author, an assistant, and Ron McKnight represented the Ministry at the sampling. Some residents were in attendance, as were two representatives of CKCO TV.

ASPHALT

Appendix I contains a discussion of the components of asphalt, differences between asphalt and coal tar and the leachability of metals and organic compounds from cured asphalt pavement.

STUDY AREA

The area in question is a typical residential area. The homes are of fairly recent construction. Except in the case of 256 Union Street, all yards have been landscaped to some degree. In the majority of cases, this has involved the application of topsoil, sod and the planting of some perennials.

In contrast, 256 Union Street at the time of sampling was not landscaped at all. Both the front and back yards were composed entirely of exposed fill which was free of both topsoil and sod. At the rear of the home there was also an open hole which was excavated to uncover sewage drainage tiles that had allegedly been damaged by shifting asphalt pieces. This hole was approximately 2.5m deep by 2.5m x 3m on the sides. Although few asphalt pieces were observed on the surface of the property at 256 Union Street, the walls of the excavation and the composite of excavated material revealed numerous asphalt fragments ranging from small gravel-sized pieces to large fragments of half a meter in diameter .

METHODOLOGY

All soil sampling was conducted in the back yards of residences from which permission was obtained. Given the profile of this issue, samples were submitted to the laboratory under a high priority submission. To accelerate the process, it was agreed by Ron McKnight and the author not to sample all properties individually. While individual samples were collected from 256 Union Street, composite samples representing equally 220, 222, 224, 228 and 232 Union Street (West Composite) and samples representing 242, 244, 248 and 254 Union Street (East Composite) were collected. Because the results of

chemical analyses of soils were compared against established guidelines to guide decisions on soil removal, off-site (control) samples were, therefore, not required for establishing the degree of contamination of the fill.

Soil sampling was conducted by the author and an assistant on September 24, 1991. All soil samples were collected in duplicate using sampling techniques appropriate for subsequent analysis of trace organic and inorganic contaminants (MOE, 1983). These techniques included the use of stainless steel soil corers and thorough between-site rinsing of all sampling equipment with distilled water, acetone and hexane. Each of the two replicate samples per location consisted of a minimum of 30 soil cores that were homogenized in the field and placed into appropriate submission containers.

Both surface soils and depth composites were collected from 256 Union Street. Surface soils (0-5cm) were collected from the rear (north) portion of the backyard. While this area had not been affected by the excavation mentioned earlier, it was extensively used by two leashed dogs. Composite depth samples (25-150cm) were also collected from the northern exposed face of the backyard excavation on the property. Surface soil composites (East and West Union St.) were also collected from the additional residences requesting sampling along the street. While the larger asphalt fragments were removed from the samples, small fragments were noticeable in surface and sub-surface samples collected from 256 Union Street. Fragments did not appear to be present in the East and West surface soil composites.

Soil samples were transported in coolers and stored frozen. Samples to be submitted for inorganic analysis were air dried, pulverized to pass through a 45 mesh sieve (thus removing the majority of the asphalt fragments) and stored in glass bottles. Samples to be analyzed for trace organic contaminants were kept frozen and not sieved or processed further (thus leaving any asphalt fragments in the sample). Organic analyses were conducted at the MOE Organic Trace Contaminants Laboratory. The samples were analyzed for 16 PAH compounds plus a total organic solvent extract. Analyses were conducted for a variety of metals in both hot acid extractions (bulk analysis) and in dilute acetic acid leachate (leachate analysis). The metals that were scanned for both bulk and leachate analysis included Cu, Ni, Pb, Zn, Fe, Mn, Al, Ba, Be, Cd, Co, Cr, Mo, Sr, Ti and V. Electrical conductivity (EC) and pH were also determined for each soil sample. All samples were forwarded to the Ministry of the Environment laboratory in Rexdale for chemical analysis.

RESULTS AND DISCUSSION

The results of the bulk inorganic soil analysis are summarized in Table 1. Of the 16 inorganic elements, only Cu, Pb, Zn and Sr were marginally elevated in the soil collected from 256 Union Street relative to composite samples collected from other residences on Union Street. In addition, concentrations of these elements tended to be slightly higher in the depth composites than in surface soils collected from 256 Union Street. However, in all cases the concentrations of these and other metals tested were well below the Phytotoxicology Upper Limit of Normal (ULN) guidelines (MOE, 1989a) (see Appendix II) and the MOE Clean-up Guidelines for Soils-Guidelines for the Decommissioning and Clean-up of Sites in Ontario (MOE, 1989b). In fact, the concentrations detected in soil from these Union Street residential properties were generally lower than those usually encountered in an urban environment. Therefore, based on bulk soil metal analysis, these soils would not be considered contaminated and could remain on site.

The results of pH and EC analysis are also summarized in Table 1. The pH results for all soils fell well within the normal range. However, notable was the elevated EC (in a 2:1 water soil extract) for sub-surface soils (mean of 2.15 mS/cm) collected from 256 Union Street. The EC is a measure of the total salts in the soil and the guidelines have been established to protect plant life. Ontario Ministry of Agriculture and Food (OMAF) (OMAF, 1988) data suggest that severe damage will result to most plants growing in soils exceeding EC readings of 1.00 mS/cm (2:1 water soil extract). Currently no MOE guideline exists for EC in a 2:1 water soil mixture. The current Decommissioning guideline of 2 mS/cm for saturation extracts would be the approximate equivalent of 0.66 mS/cm for the 2:1 mixture (University of Guelph, unpubl.). Therefore, based on phytotoxicological considerations and limited sub-surface soil sampling at 256 Union Street, it may be concluded that sub-surface fill on the property is contaminated with salt-like material. This is based on the exceedence of both the OMAF plant response information and the modified Decommissioning guideline for EC.

The elevated EC was not likely the result of material leached from asphalt adhesive but may have accumulated in the asphalt matrix and/or soil beneath the road surface as the result of road salting. When the road and sub-surface were excavated for use as fill on Union Street, these accumulated salts could have accompanied the fill. It is also possible that salts contributing to the elevated EC value originated from the damaged municipal sewage tile.

If soil salts are considered a concern by the District MOE, residents of Union Street and the City of Cambridge additional work will be required to accurately determine the lateral and depth distribution of elevated salt concentrations in the imported fill. The need for additional work should consider the fact that surface soil samples were not contaminated and salt-like contamination at depth would not adversely affect vegetation growing on site.

Leachate analyses for inorganic elements are summarized in Table 2. The results indicate that for some metals, especially strontium and to a lesser degree manganese, concentrations are elevated in sub-surface soils at 256 Union Street as compared to both on and off-site surface soils. Zinc concentrations were also slightly higher for soils collected at 256 Union Street than off-site surface composites. However, as with bulk inorganic analyses, in no case did leachate metal concentrations exceed established guidelines (Regulation 309 - Schedule 4) that would have classed the material as leachate toxic waste/hazardous waste (>100 times the values in Schedule 4) or subject waste (10-100 times the values in Schedule 4).

The results of soil organic analyses are summarized in Table 3. The values are in micrograms per gram. Although there are currently no ULNs for organic compounds, the Canadian Council of Ministers of the Environment (CCME) has developed Interim Remediation Criteria for Soil (CCME, 1991) that include guidelines for nine PAHs and for total PCBs. These guidelines (residential/parkland) are also presented in Table 3.

Trace PAH concentrations in soils were detected at all sites and in both surface and sub-surface soils. Those PAHs that were consistently found in at least trace concentrations were; phenanthrene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluorene and benzo(a)pyrene. The mean concentrations of a number of PAHs were notably elevated in the depth composites collected from the 256 Union Street relative to other samples collected both on and off site. These included; benzo(g,h,i)perylene, phenanthrene, fluoranthene, pyrene, chrysene, benzo(b)fluorene, benzo(a)anthracene, benzo(k)fluoranthene, benzo(a)pyrene and indeno(1,2,3-cd)pyrene. However, in all cases, the mean PAH concentration for the depth composite was well below the value above which remediation may be required for residential and parkland uses. The elevated PAH results for the depth composite were put into question because of large discrepancies between replicate values. The concentrations of specific PAHs in Replicate 1 of the depth composite were as much as 22 times higher than in Replicate 2 of the same composite. This indicates that an asphalt fragment may have been processed along with the first replicate, or that PAHs may be associated with the sewage contamination.

The results of total PCB analyses (Table 3) clearly indicated that surface soils on Union Street and sub-surface soil of 256 Union Street were not contaminated with PCB compounds. In all cases, the total PCB concentrations for soils were below the analytical detection limit and well below any established guidelines for clean-up.

The solvent extract data are listed at the bottom of Table 3. This is a measure of the "total" soluble organic constituents. These would include anthropogenic organic contaminants as well as naturally occurring organics associated with decomposing organic matter. The highest organic solvent extract

concentration (2520 ppm) occurred for soils collected from the depth composite at 256 Union Street. Unlike the results for PAHs, the solvent extract concentrations were similarly high for both replicate samples. Therefore, PAHs are not likely a significant contribution to the higher total organic solvent extract concentration in the sub-surface soil samples. It is probable that elevated solvent extractables in the sub-surface soils collected from the face of the excavation resulted from discharge associated with the damaged sewage tile.

SUMMARY

The asphalt component of material used as fill for a row housing development on Union Street may have contributed to trace concentrations of PAH compounds in sub-surface and, to a lesser degree, surface soils. However, the exposure to PAHs from buried, weathered asphalt would be environmentally inconsequential relative to PAHs associated with newer, exposed asphalt in nearby driveways, parking lots and roads. Regardless, in every case, PAH concentrations were well below concentrations at which remediation may be required for residential and parkland uses. Similarly, analyses for a variety of metals in both hot acid bulk extractions and dilute acid leachate did not indicate that soils had been contaminated or that they need be removed from the site. Electrical conductivity readings of sub-surface soils did indicate that salt concentrations of soils collected from 256 Union Street were excessive for plant growth. The most likely explanations for elevated salt concentrations are historical exposure of the asphalt fill material to road salt or sewer discharge.

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Table 1

Results¹ of Inorganic Analysis of Soil Samples Collected from Residential Properties on Union Street, Cambridge, Ontario, September 24, 1991.

Element	256 Union Street		East Union Street	West Union Street	Phytotoxicity ULN ²	Clean-Up Guideline ³
	Surface	Depth Composite				
	Mean	Mean	Mean	Mean		
Cu	19	21	12	10	100	200
Ni	6.7	8.1	8.2	6.7	60	200
Pb	27	40	22	24	500	500
Zn	105	110	75	73	500	800
Fe	12000	13000	13000	12000	35000	NA
Mn	420	450	430	340	700	NA
Al	9400	8400	10000	9700	NA	NA
Ba	45	41	46	46	NA	NA
Be	0.7 ^{<T}	0.4 ^{<T}	0.4 ^{<T}	0.4 ^{<T}	NA	NA
Cd	1.0 ^{<W}	1.0 ^{<W}	1.0 ^{<W}	1.0 ^{<W}	4	4
Co	3.2 ^{<T}	3.6 ^{<T}	3.4 ^{<T}	3.0 ^{<T}	25	50
Cr	12	11	13	12	50	1000
Mo	1 ^{<W}	1 ^{<W}	1 ^{<W}	1 ^{<W}	3	5
Sr	28	90	23	25	NA	NA
Ti	190	200	200	120	NA	NA
V	23	24	26	23	70	NA
pH	6.6	6.8	6.9	6.1	NA	6-8
EC ⁴ (mS/cm)	0.3	2.2	0.4	0.3	NA	0.66 ⁵

¹ Parts per million (ppm). Results are means of duplicate sample analyses.

² Phytotoxicology Upper Limit of Normal (ULN) for urban soils, see attached appendix.

³ MOE Clean-up Guidelines for Soils-Guidelines for the Decommissioning and clean-up of sites in Ontario. All units in ppm.

⁴ EC = electrical conductivity (2:1 water:soil paste).

⁵ Guideline based on conversion of Decommissioning Guideline for EC to compensate for difference in method. Decommissioning Guideline (2 mS/cm) based on saturation extract. Saturation extract conductivity to 2:1 water:soil paste conductivity ratio is approximately 3:1 (University of Guelph, unpbl.).

^{<T} A measurable trace amount. Interpret with caution.

^{<W} Less than the reported value. No measurable response (zero).

NA ULN not established.

Table 2

Results¹ of Inorganic Leachate Analysis of Soil Samples Collected from Residential Properties on Union Street, Cambridge, Ontario, September 24, 1991.

Element	256 Union Street		East Union Street	West Union Street	Regulation 309 Schedule 4 ²	
	Surface	Depth Composite			Hazardous Waste	Subject Waste
	Mean	Mean	Mean	Mean		
Cu	0.085	0.009	0.028	0.008	NA	NA
Ni	0.001 ^{<w}	0.004 ^{<T}	0.001 ^{<w}	0.001 ^{<w}	NA	NA
Pb	0.019	0.020	0.074	0.005	>5	0.5-5
Zn	0.076	0.092	0.045	0.019	NA	NA
Fe	0.01 ^{<T}	0.01 ^{<T}	0.13	0.044	NA	NA
Mn	0.02	5.0	5.8	0.86	NA	NA
Al	0.07	0.11	0.19	0.13	NA	NA
Ba	0.18	0.40	0.30	0.29	>100	10-100
Be	0.0003	0.0004	0.0004	0.0003	NA	NA
Cd	0.0047	0.0002 ^{<w}	0.0002 ^{<w}	0.0002 ^{<w}	>0.5	0.05-0.5
Co	0.0005 ^{<w}	0.0005 ^{<w}	0.0010 ^{<T}	0.0005 ^{<w}	NA	NA
Cr	0.001 ^{<w}	0.001 ^{<w}	0.001 ^{<w}	0.001 ^{<w}	>5	0.5-5
Mo	0.0039	0.0005 ^{<w}	0.0021 ^{<T}	0.0005 ^{<w}	NA	NA
Sr	0.68	4.0	0.73	0.85	NA	NA
Ti	0.0005 ^{<w}	0.0005 ^{<w}	0.0005 ^{<w}	0.0005 ^{<w}	NA	NA
V	0.0018 ^{<T}	0.0005 ^{<w}	0.0005 ^{<w}	0.0005 ^{<w}	NA	NA

¹ Results are means of duplicate sample analyses and in mg/L.

² Concentrations of inorganic contaminants (mg/L) resulting in classification of material as a waste as per Schedule 4 of Regulation 309.

NA Regulation 309-Schedule 4 leachate quality criteria not available.

<T A measurable trace amount. Interpret with caution.

<w Less than the reported value. No measurable response (zero).

Table 3

Results¹ of PAHs and PCB Analyses of Soil Samples Collected from Residential Properties on Union Street, Cambridge, Ontario, September 24, 1991.

Element	256 Union Street		East Union Street	West Union Street	CCME Guidelines ² (Residential/Parkland)
	Surface	Depth Composite			
	Mean	Mean	Mean	Mean	
<u>PAHs</u>					
Dibenzo(a,h)anthracene	0.02 ^{<w}	0.04 ^{<w}	0.02 ^{<w}	0.02 ^{<w}	1
Benzo(g,h,i)perylene	0.04 ^{<w}	0.10	0.02 ^{<w}	0.02 ^{<w}	NA
Napthalene	0.01 ^{<w}	0.01 ^{<w}	0.01 ^{<w}	0.01 ^{<w}	5
Acenaphthylene	0.01 ^{<w}	0.02 ^{<w}	0.01 ^{<w}	0.01 ^{<w}	NA
Acenaphthene	0.01 ^{<w}	0.01 ^{<w}	0.01 ^{<w}	0.01 ^{<w}	NA
Fluorene	0.01 ^{<w}	0.01 ^{<w}	0.01 ^{<w}	0.01 ^{<w}	NA
Phenanthrene	0.07 ^{<t}	0.22	0.03 ^{<t}	0.09 ^{<t}	5
Anthracene	0.02 ^{<w}	0.04 ^{<t}	0.02 ^{<w}	0.02 ^{<t}	NA
Fluoranthene	0.17	0.89	0.06 ^{<t}	0.13 ^{<t}	NA
Pyrene	0.13 ^{<t}	0.97	0.05 ^{<t}	0.10 ^{<t}	10
Benzo(a)anthracene	0.07 ^{<t}	0.58	0.03 ^{<t}	0.06 ^{<t}	1
Chrysene	0.08 ^{<t}	0.59	0.04 ^{<t}	0.06 ^{<t}	NA
Benzo(k)fluoranthene	0.06 ^{<t}	0.36	0.02 ^{<w}	0.04 ^{<t}	1
Benzo(b)fluorene	0.06 ^{<t}	0.33	0.03 ^{<t}	0.04 ^{<t}	NA
Benzo(a)pyrene	0.06 ^{<t}	0.38	0.03 ^{<t}	0.05 ^{<t}	1
Indeno(1,2,3-cd)pyrene	0.04 ^{<w}	0.17	0.02 ^{<w}	0.02 ^{<w}	1
<u>PCB</u>					
Polychlorobiphenyls (total)	0.01 ^{<w}	0.01 ^{<w}	0.01 ^{<w}	0.01 ^{<w}	5
<u>Other</u>					
Total Organic Solvent Extract	441	2520	338	514	NA

¹ Results are means of duplicate sample analyses and in ug/g.

² Canadian Council of Ministers of the Environment (CCME) Interim Remediation Criteria for Soil.

<^t A measurable trace amount. Interpret with caution.

<^w Less than the reported value. No measurable response (zero).

NA CCME Guideline not established.

Composition and Leachability of Asphalt

Asphalt is derived from crude petroleum oil which is a mixture of aromatic hydrocarbons, paraffin and cycloparaffins. Small quantities of organic compounds containing sulphur, iron, nickel, vanadium and other metals are also found in crude oil. Asphalt is produced by the evaporation of lighter hydrocarbons of the crude oil and partial oxidation of the residue and does not involve cracking or thermal conversion. There are at least three general categories of manufacturing processes available for the production of asphalt, depending on the type of crude available and the desired characteristics of the material. The variations in petroleum source and composition, manufacturing technique and blending, make generalizations concerning chemical composition difficult. It is also important to distinguish between petroleum asphalt and coal-tar products, which are distinctly different in their raw material source (crude oil vs. coal), manufacturing process and resulting chemical composition. Many of the current guidelines concerning polycyclic aromatic hydrocarbon (PAH) contamination have been developed to address problems on sites contaminated with coal tar residues (Puzinauskas and Corbett, 1978).

An important difference between coal tar and asphalt chemistry is the proportion of total carbon found in aromatic rings. Asphalt typically contains about 40 percent of total carbon as aromatic rings compared with 80 percent for coal tar (Puzinauskas and Corbett, 1978). Coal tar also contains a higher fraction of compounds of lower molecular weight. Distillation during asphalt manufacturing is thought to remove the majority of 4-7 fused-ring polynuclear aromatics, including the known PAH carcinogens (King *et al.*, 1981). However, Wallcave *et al.* (1971) found small but detectable levels of at least four known carcinogenic PAHs in hot mix asphalt [ie. benzo(a)anthracene (5.7 ppm), benzo(a)pyrene (4.9 ppm), benzo(e)pyrene (10.4 ppm) and indeno(1,2,3,-cd)pyrene (trace)]. The corresponding concentrations of these PAHs in coal tar pitch were 10700 ppm, 10450 ppm, 6200 ppm and 8300 ppm, respectively.

The suitability of recycled asphalt pavement (RAP) as "clean" fill has not been fully researched. However, a recent study conducted by the Heritage Research Group examined PCBs and PAHs, semivolatile organics and metals in the leachate of RAP (Kriech, 1991). No PCBs or semivolatile organics were found in the leachate of RAP tested at the laboratory detection limits. PAHs were detected at only trace concentrations (naphthalene the highest at 0.0004 ppm) and well within US guidelines. Metals were detected in some samples (eg. barium, chromium and lead). The study concluded that RAP would appear to meet the US TCLP (Toxic Characteristic Leachability Procedure) maximum concentration guidelines and would, therefore, not be of concern for use as clean fill.

APPENDIX II

Derivation and Significance of the MOE Phytotoxicology "Upper Limits of Normal" Contaminant Guidelines

The MOE Upper Limits of Normal (ULN) contaminant guidelines represent the expected maximum concentration in surface soil, foliage (trees and shrubs), grass, moss bags, and snow from areas in Ontario not exposed to the influence of a point source of pollution. Urban ULN guidelines are based on samples collected from developed urban centres, whereas rural ULN guidelines were developed from non-urbanized areas. Samples were collected by Phytotoxicology staff using standard sampling procedures (ref: Ontario Ministry of the Environment 1983, *Phytotoxicology Field Investigation Manual*). Chemical analyses were conducted by the MOE Laboratory Services Branch.

The ULN is the arithmetic mean, plus three standard deviations of the mean, of the suitable background data. This represents 99% of the sample population. This means that for every 100 samples which have not been exposed to a point source of pollution, 99 will fall within the ULN.

The ULNs do not represent maximum desirable or allowable limits. Rather, they are an indication that concentrations that exceed the ULN may be the result of contamination from a pollution source. Concentrations that exceed the ULNs are not necessarily toxic to plants, animals, or people. Concentrations that are below the ULNs are not known to be toxic.

ULNs are not available for all elements. This is because some elements have a very large range in the natural environment and the ULN, calculated as the mean plus three standard deviations, would be unrealistically high. Also, for some elements, insufficient background data is available to confidently calculate ULNs. The MOE Phytotoxicology ULNs are constantly being reviewed as the background environmental data base is expanded. This will result in more ULNs being established and may amend existing ULNs.

